Thermodynamic Views of the Principle of Le Chatelier

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Abstract

The effect of temperature change on a chemical equilibrium is discussed on the basis of both Le Chatelier's principle and thermodynamics. Furthermore, some misleading ideas that may arise from using the standard Gibbs free energy change, ΔG°, to predict how the chemical equilibria are shifted by temperature are discussed.

Introduction

Some authors occasionally are not careful about the basic sdifference between free energy change, ΔG, of a reaction and the standard free energy change, ΔG°, for the reaction under consideration, and they sometimes use ΔG° instead of ΔG to predict the direction of spontaneous changes. It is obvious that, at constant temperature and pressure, the spontaneity of a given reaction could be determined by the sign of ΔG only and not ΔG°. Indeed, ΔG° values are only used to determine the values of thermodynamic equilibrium constants at constant temperature and pressure.

Furthermore, in order to predict how a chemical equilibrium is shifted when the temperature is increased we should use $\Delta G^\circ/T$, not just ΔG°, otherwise, incorrect results which are not in accordance with Le Chatelier's principle may be obtained.

In this paper, these points are discussed thermodynamically.

Discussion

Reviewing some general texts abouts chemical thermodynamics, it is seen that ΔG° is sometimes used instead of ΔG in order to predict the reaction spontaneity (1,2,3,4). It can be shown that using ΔG° in this way, may lead to misleading results. Indeed ΔG which represents the Gibbs free energy change of a reaction at any concentration of

ants and products and at constant temperature
pressure can only be used to predict the on spontaneity. On the basis of the second of thermodynamics, if $\Delta G_{T,P}<O$, then the on is spontaneous, but, if $\Delta G_{T,P} = O$, then action is in equilibrium.

the other hand, ΔG° which represents the ard Gibbs free energy change for the ard reaction should be distinguished from nd it should be noted that its values are to nine the magnitudes of thermodynamic orium constants.

nerally, ΔG° alone can not be a criterion for tion of the spontaneity of a reaction. For ce, it happens that ΔG° of a reaction has a e sign, while for the same P & T but nt concentrations, ΔG of the same reaction ve a negative sign (5).

eaction as $aA + bB \rightleftharpoons cC + dD$

ation between ΔG and ΔG° at constant ature is given by

$$\Delta G^\circ + RT \ \ln \ Q_a \qquad (1)$$

Q_a the reaction quotient, is given by:

$$\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

ibrium we have $\Delta G = O$; So

$$-\Delta G^\circ = RT \ \ln \ K_{th} \qquad (2)$$

where K_{th} is called the thermodynamic equilibrium constant of the reaction,

$$K_{th} = \left\langle \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} \right\rangle \qquad (3)$$

One may apparently conclude from equation (2) that both K_{th} and $-\Delta G^\circ$ change in the same direction; For example, any factor that could increase $-\Delta G^\circ$ would increase K_{th} also, or vice versa. This certainly leads to a misleading conclusion (6,7,8). In order to illustrate this statement, we consiedr a reaction with $\Delta H^\circ > O$ and $\Delta S^\circ < O$ which both are temperature independent. At these conditions, an increase in temperature will also increase the value of ΔG° (or decrease the value of $-\Delta G^\circ$).

$$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_p = -\Delta S^\circ$$

Considering this result, one may apparently conclude that K_{th} should decrease as ΔG° increases, but this conclusion is exactly a contradiction with Le Chatelier's principle. According to the Le Chatelier's principle, in the case of an endothermic reaction, the value of K_{th} will increase as temperature is raised. Certainly, the prediction which is based on the Le Chatelier's principle is correct, so to demonstrate this apparent contradiction we chould carefully look at equation (2). As it can be seen, the variation of $-\Delta G^\circ$ is related to the variation of both T and in $\ln K_{th}$. Therefore, a slight rearrangement of equation (2) gives

$$\frac{-\Delta G^\circ}{RT} = \ln K_{th} \quad (4)$$

or

$$\frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = \ln K_{th} \quad (5)$$

Equations(2-5) show clearly that if $\Delta H^\circ > O$ and $\Delta S^\circ < O$, then $\frac{-\Delta G^\circ}{T}$ will increase as temperature is raised and, therefore, $\ln K_{th}$ (and K_{th} thereby) also will increase with temperature.

Eventhough the value of $-\Delta G^\circ$ uneder these conditions is decreased as temperature is raised, but on the contrary, the value of $\frac{-\Delta G^\circ}{T}$ is increased when temperature goes up, which implies that the value of equilibrium constant, K_{th}, increases by increasing temperature:

$$-\left(\frac{\partial(\Delta G^\circ/T)}{\partial T}\right)_p = +\frac{\Delta H^\circ}{T^2}$$

Therefore, in order to predict how the chemical equilibria are shifted by temperature, we should use $\frac{-\Delta G^\circ}{T}$, not just $-\Delta G^\circ$ (9).

As an additional support to our comment, one can refer to the following equations (10).

$$\frac{-\Delta G^\circ}{T} = \Delta S^\circ_{total} \quad (6)$$

$$\frac{-\Delta G}{T} = \Delta S_{total} \quad (7)$$

Since, on the basis of the second law of thermodynamics which states the spontaneous processes occur in direction of increasing total entropy , the quantities $\frac{-\Delta G}{T}$ and $\frac{-\Delta G^\circ}{T}$ are appropriate to predict the spontaneous direction of the chemical reactions and how the chemical equilibria are shifted by temperature,resspectively.

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